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(71) Applicant(s)

Commonwealth Scientific and Industrial Research  
Organization  
(Incorporated in Australia)  
Limestone Avenue, Campbell,  
Australian Capital Territory 2601, Australia

(72) Inventor(s)

Jonathan Howard Hodgkin  
Hans Jorg Grlessner  
Thomas Reinhold Gengenbach

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(56) Documents Cited by ISA

EP 0176636 A1 WO 91/16378 A WO 89/11500 A  
AU 910073964 A JP 058008517 A JP 002022339 A  
US 5494712 A

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(74) Agent and/or Address for Service

Elkington and Fife  
Prospect House, 8 Pembroke Road, SEVENOAKS,  
Kent, TN13 1XR, United Kingdom

(54) Abstract Title

Method for reducing crazing in a plastics material

(57) A method for reducing crazing in a plastics material characterised in that it comprises the steps of: (1) cleaning the surface of the material; and (2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.

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<p>(21) International Application Number: PCT/AU97/00101</p> <p>(22) International Filing Date: 21 February 1997 (21.02.97)</p> <p>(30) Priority Data: PN 8203 21 February 1996 (21.02.96) AU</p> <p>(71) Applicant (for all designated States except US): COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): HODGKIN, Jonathan, Howard [AU/AU]; 28 Celia Street, Burwood, VIC 3125 (AU). GRIESSER, Hans, Jorg [AU/AU]; 20 View Road, The Patch, VIC 3792 (AU). GENGENBACH, Thomas, Reinhold [DE/AU]; 3 Mount Street, Glen Waverley, VIC 3150 (AU).</p> <p>(74) Agents: CORBETT, Terence, G. et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).</p>			
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(54) Title: METHOD FOR REDUCING CRAZING IN A PLASTICS MATERIAL

**(57) Abstract**

A method for reducing crazing in a plastics material characterised in that it comprises the steps of: (1) cleaning the surface of the material; and (2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.

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## METHOD FOR REDUCING CRAZING IN A PLASTICS MATERIAL

The present invention relates to a method for reducing crazing in a plastics material, in particular a transparent plastics material.

5

When transparent plastics materials are used for windows, roofing, signs or light fittings maintenance of their original optical clarity is important. Unfortunately, under the influence of environmental factors such as light, heat and moisture many plastics materials suffer from crazing. Crazing is a phenomenon where microvoids form in the body of the materials. These 10 microvoids may not cause a significant deterioration in mechanical strength of the article, but they do reflect/refract light and decrease the clarity of the article. Ultimately, crazing decreases the strength of the article and can lead to failure.

As crazing is a visually obvious deterioration in the material, it gives an impression of 15 poor quality or lack of maintenance which is particularly objectionable in applications where visual clarity is desired. Such applications include the windows of transport vehicles, roofing sheets, light fittings or signs. Many signs are made of transparent materials with the graphic material applied to the underside to be viewed through the material. Crazing in vehicle windows interferes with the vision of the occupants decreasing their enjoyment of the journey and may 20 even pose a real safety hazard. Crazing is particularly objectionable in aircraft windows and frequently causes the replacement, at a great expense, of windows which are otherwise sound and serviceable. As a consequence of the crazing problem, the use of glass windows is being considered for aircraft despite the weight penalty that this would impose.

25 The cause of crazing is unknown and may be manifold. It is thought that one cause is the diffusion of small molecules such as water or surfactants into the material which decreases the attractive forces between polymer chains and allows movement of molecules under internal or external stress thus forming microvoids.

30 According to the present invention there is provided a method for reducing crazing in a plastics material which comprises the steps of:

- (1) cleaning the surface of the material; and

(2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.

The method of the present invention may be used to reduce crazing in a wide variety of 5 plastics materials, such as, for example, acrylics, styrenes, polycarbonates, polyesters or polyurethanes. The plastics material may be an article which is preferably in the form of a laminate or sheet. The method will have particular value when applied to transparent plastics material where visual clarity is important. Examples of transparent materials include acrylic or polycarbonate sheets as used for the windows of transport vehicles such as aircraft, boats, trains 10 and motor vehicles, signs or for architectural uses such as in roofing, glazing sheets and light fittings.

The material may be cleaned in step (1) by any method which leaves the surface substantially free of any contamination capable of interfering with the adhesion of the plasma 15 polymer coating. A preferred method of cleaning the surface is to subject the material to a low pressure plasma of an inert gas such as argon, neon, or nitrogen. Another preferred method of cleaning the surface involves subjecting the material to a low pressure plasma of an oxidising gas such as air or oxygen. Water vapour is also a suitable oxidising gas for this purpose. These cleaning methods may be advantageously carried out in the same apparatus which is used in step 20 (2) of the method.

The monomer used in step (2) may be any saturated or unsaturated organic compound capable of producing a coating of a substantially non-oxidising polymer containing organic groups.

25

Suitable saturated monomers include siloxanes, fluorinated compounds, lower hydrocarbons, lower alcohols, lower alkylamines and mixtures thereof. The term "lower" as used herein refers to monomers containing 1 to 12 carbon atoms.

30 Suitable unsaturated monomers include acrylic esters, methacrylic esters, vinyl esters, vinyl aromatics, unsaturated or polyunsaturated hydrocarbons and mixtures thereof. Examples of these monomers include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate,

methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, 2-ethylhexyl methacrylate, vinyl acetate, styrene, *p*-chloromethylstyrene, 2-vinylpyridine, 4-vinylpyridine, N-vinylpyrrolidone, vinyl halides of the formula  $\text{CH}_2=\text{CHX}$  wherein X is Cl or F, vinylidene halides of the formula  $\text{CH}_2=\text{CX}_2$  wherein X is independently Cl or F, vinyl ethers of the formula  $\text{CH}_2=\text{CHOR}$  wherein R is alkyl, and allyl derivatives such as allyl ethers, allyl carbonates or diallyl carbonates.

Plasma polymers from some of these monomer classes typically undergo extensive oxidation on aging (Gegennbach *et al*, *J Polymer Sci, Part A Polymer Chemistry*, **32**, 1399-1414 (1994); Gegennbach *et al*, *Surface Interface Analysis*, in press 1996). In those cases it is necessary to carefully adjust the plasma deposition parameters until minimal oxidation following ageing in the air is obtained. While substantial oxidation can occur in plasma polymers without affecting their structural integrity, minimal oxidation lessens the danger of adverse changes to the surface or mechanical properties of a plasma polymer as it ages. As used herein, the term "substantially non-oxidising polymer" refers to materials which show such minimal oxidation.

15

It has been found that for windows made from acrylic polymers such as those used in aircraft, the substantially non-oxidising polymer coating is preferably hydrophobic. Siloxanes or perfluorinated compounds are particularly suitable monomers for producing hydrophobic coatings provided that the resulting polymer contains some organic groups. Examples of such monomers include hexamethyldisiloxane, vinyltrimethoxysilane, perfluorocyclohexane and tetrafluoroethylene.

For plastics materials where the crazing is caused by exposure to hydrophobic molecules such as petroleum products, a hydrophilic coating may be more suitable in which case monomers such as alcohols or alkylamines may be used. Preferred examples of such monomers include methanol, ethanol and the various isomers of propanol or butanol.

The plasma polymer coatings produced by the method of this invention are usually highly crosslinked and hence stable. They may also be abrasion resistant.

30

Many of the materials to which the method of the present invention can be applied are subject to varying stresses in service and move or flex slightly as a consequence. Accordingly,

there is a need to match the mechanical compliance of the coating with that of the material. The present invention achieves this by ensuring that the plasma polymer coating applied in step (2) is thin and adheres well to the material so that it moves with the material without itself cracking or crazing. It is preferred that the plasma polymer coating has a thickness of about 2 to about 5 500 nm, more preferably about 5 to about 50 nm.

The prior art methods produce thicker coatings which are unable to follow the movement of the material and crack and/or delaminate.

10 The method of the present invention may be carried out in any suitable apparatus for performing plasma polymerisation such as that described in AU 654131. AU 654131 describes a process for plasma coating polymeric materials in a vapour of an amide monomer so as to provide a coating suitable for the growth of cells on biomedical implants to be administered into the human body. Preferably, low pressure plasma polymerisation is employed in which the 15 pressure is about 0.5 to about 1.0 torr.

The present invention also provides a craze resistant article comprising a plastics material having a thin coating of a substantially non-oxidizing plasma polymer containing organic groups.

20 This invention is further explained and illustrated in the following non-limiting examples.

### Example 1 - Coating of acrylic plastic sheet

Test strips of 35 cm x 3 cm were cut from a 3 mm thick acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues and repeated twice further with fresh tissues. The final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

0.55 Torr pressure of air

225 kHz frequency

10 Watt load power

60 secs duration.

The coating was applied to the air plasma cleaned sample by exposure to a plasma in hexamethyl disiloxane vapour under the following conditions:

15

0.11 Torr pressure

225 kHz frequency

50 Watt load power

240 secs duration.

20.

A strong adherent coating of plasma polymer was formed.

### Example 2 - Evaluation of effect of coatings on craze resistance

25 Test strips prepared according to Example 1 were tested for susceptibility to crazing using a modification of the cantilever test method of Burchill, Mathys and Stacewicz (*J. Materials Science* 22, 483-487 (1987)) which is a modification of the standard test method ANSI/ASTM F484-77 "Stress crazing of acrylic plastics in contact with liquid or semi-liquid compounds". The samples were 35 cm long. A weight of 1 kg was suspended from the  
30 unsupported end of the test strip. The load was applied for 10 mins before placing the test fluid (iso-propanol) on the tensile surface which was kept wet until examination for crazing (at least a further 20 mins).

Uncoated control strips cut from the same sheet crazed within 20 mins. However, the strips prepared in Example 1 did not craze after 6 hrs when the test was halted.

**EXAMPLE 3 - Coating of Commercial Acrylic Sheet with n-heptylamine polymer after 5 air plasma cleaning**

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an 10 air plasma under the following conditions:

0.50 Torr pressure  
200 kHz frequency  
10 Watt load power  
15 60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-heptylamine vapour under the following conditions:

20 0.40 Torr pressure  
200 kHz frequency  
10 Watt load power  
180 second duration.

25 A coating of plasma polymer ca 120 nm thick formed.

**EXAMPLE 4 - Coating of Commercial Acrylic Sheet with n-heptylamine polymer after argon plasma cleaning**

30 Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an

argon plasma under the following conditions:

5            0.50 Torr pressure  
          200 kHz frequency  
          10 Watt load power  
          60 second duration.

10            The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-heptylamine vapour under the following conditions:

15            0.40 Torr pressure  
          200 kHz frequency  
          20 Watt load power  
          180 second duration.

20            A coating of plasma polymer ca 110 nm thick formed.

**EXAMPLE 5 - Coating of Commercial Acrylic Sheet with n-hexane polymer after air plasma cleaning**

25            Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

30            0.50 Torr pressure  
          200 kHz frequency  
          10 Watt load power  
          60 second duration.

35            The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-hexane vapour under the following conditions:

0.11 Torr pressure  
200 kHz frequency  
20 Watt load power  
120 second duration.

5

A coating of plasma polymer ca 140 nm thick formed.

**EXAMPLE 6 Coating of commercial acrylic sheet with n-hexane polymer after argon plasma cleaning**

10

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an argon plasma under the following conditions:

15

0.50 Torr pressure  
200 kHz frequency  
10 Watt load power  
60 second duration.

20

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-hexane vapour under the following conditions:

25

0.40 Torr pressure  
200 kHz frequency  
20 Watt load power  
120 second duration.

A coating of plasma polymer ca 130 nm thick formed.

30

## EXAMPLE 7 - Coating of commercial acrylic sheet with methanol polymer after air plasma cleaning

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.

5 Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

0.50 Torr pressure

### 10 200 kHz frequency

10 Watt load power

60 second duration.

60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in 15 methanol vapour under the following conditions:

0.60 Torr pressure

200 kHz frequency

20 Watt load power

20 600 second duration.

A coating of plasma polymer ca 51 nm thick formed.

## EXAMPLE 8 Coating of commercial acrylic sheet with perfluorodimethylcyclohexane polymer after air plasma cleaning

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.

5 Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

0.50 Torr pressure

10 200 kHz frequency

10 Watt load power

60 second duration.

60 second duration.

60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in

15 perfluorodimethylcyclohexane vapour under the following conditions:

0.2 Torr pressure

200 kHz frequency

5 Watt load power

20 180 second duration.

A coating of plasma polymer ca 120 nm thick formed.

**EXAMPLE 9 - Coating of commercial acrylic sheet with methyl methacrylate polymer**  
25 **after air plasma cleaning**

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

0.50 Torr pressure

200 kHz frequency  
10 Watt load power  
60 second duration.

5 The coating was applied to the plasma-cleaned sample by exposure to a plasma in methyl methacrylate vapour under the following conditions:

10 0.5 Torr pressure  
200 kHz frequency  
10 Watt load power  
60 second duration.

A coating of plasma polymer ca 210 nm thick formed.

15 **EXAMPLE 10 - Coating of commercial acrylic sheet with n-butyl methacrylate polymer after air plasma cleaning**

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.  
20 Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

25 0.50 Torr pressure  
200 kHz frequency  
10 Watt load power  
60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-butyl methacrylate vapour under the following conditions:

0.5 Torr pressure

200 kHz frequency  
5 Watt load power  
120 second duration.

5 A coating of plasma polymer ca 125 nm thick formed.

**EXAMPLE 11 - Evaluation of effect of coatings on craze resistance to polar materials.**

10 Test strips prepared according to Examples 3 - 10 were tested for susceptibility to crazing using a modification of the cantilever test method of Example 2. The samples were 35 cm long and a weight of 1 kg was suspended from the unsupported end of the test strip. The load was applied and the test fluid (isopropanol) applied immediately to the tensile surface which was kept wet and under observation until crazing occurred.

15 Although all test strips eventually crazed, all treated strips lasted at least ten times longer than uncoated control strips.

These results demonstrate that the process of the invention enhances the craze resistance  
20 of commercial acrylic sheet such as that used for glazing or signs as well as the stretched acrylic sheet used for aircraft windows.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the  
25 inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

## CLAIMS

1. A method for reducing crazing in a plastics material characterised in that it comprises the steps of:
  - 5 (1) cleaning the surface of the material; and
  - (2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.
2. A method as claimed in Claim 1, characterised in that the monomer in step (2) is a saturated or unsaturated organic compound capable of producing a coating of a substantially non-oxidising polymer containing organic groups.
- 10 3. A method as claimed in Claim 2, characterised in that the monomer is a saturated monomer selected from the group consisting of siloxanes, fluorinated compounds, lower hydrocarbons, lower alcohols, lower alkylamines and mixtures thereof.
- 15 4. A method as claimed in Claim 2, characterised in that the monomer is an unsaturated monomer selected from the group consisting of acrylic esters, methacrylic esters, vinyl esters, vinyl aromatics, unsaturated or polyunsaturated hydrocarbons and mixtures thereof.
- 20 5. A method as claimed in Claim 4, characterised in that the monomer is selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, 2-ethylhexyl methacrylate, vinyl acetate, styrene, *p*-chloromethylstyrene, 2-vinylpyridine, 4-vinylpyridine, N-vinylpyrrolidone, vinyl halides of the formula  $\text{CH}_2=\text{CHX}$  wherein X is Cl or F, vinylidene halides of the formula  $\text{CH}_2=\text{CX}_2$  wherein X is independently Cl or F, vinyl ethers of the formula  $\text{CH}_2=\text{CHOR}$  wherein R is alkyl, and allyl derivatives such as allyl ethers, allyl carbonates or diallyl carbonates.
- 30 6. A method as claimed in Claim 1 or Claim 2, characterised in that the plastics material is an acrylic polymer and the polymer coating is a siloxane or perfluorinated compound.

7. A method as claimed in Claim 6, characterised in that the polymer is produced from a monomer selected from the group consisting of hexamethyldisiloxane, vinyltrimethoxysilane, perfluorocyclohexane and tetrafluoroethylene.
- 5 8. A method as claimed in Claim 1 or Claim 2, characterised in that the plastics material is to be used in an environment where it is exposed to hydrophobic molecules and the polymer coating is a hydrophilic coating.
9. A method as claimed in Claim 8, characterised in that the polymer is produced from a monomer produced from an alcohol or alkylamine.
10. A method as claimed in Claim 9, characterised in that the polymer is produced from an alcohol selected from the group consisting of methanol, ethanol and the various isomers of propanol or butanol.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00101

## A. CLASSIFICATION OF SUBJECT MATTER

Int Cl<sup>6</sup>: C08F 2/52 C08J 7/04 7/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F 2/52 C08J 7/04 7/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT: (CRAZ: OR CRACK:) and (PLASMA or ION: or DISCHARG:) and IPC as above

JAPIO: as above for WPAT CASM: (CRAZ: or CRACK:) and PLASMA and PLASTIC:

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91/16378 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 31 October 1991 Entire document	1-10
A	AU 73964/91 A (THE GOODYEAR TIRE & RUBBER COMPANY) 3 October 1991 Entire document	1-10



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9 April 1997

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International Application No.

PCT/AU 97/00101

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 89/11500 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 30 November 1989 Entire document	1-10
A, P	US 5494712 A (ING-FENG HU et al) 27 February 1996 Entire document	1-10
A	EP 176636 A1 (JAPAN SYNTHETIC RUBBER CO. LTD) 9 April 1986 Entire document	1-10
A	JP 02022339 A (HITACHI CABLE KK) 25 January 1990 Derwent Abstract Accession No 90-070437 Abstract	1-10
A	JP 58008517 A (SUMITOMO DENKI KOGYO KK) 18 January 1983 Abstract	1-10

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00101

## Information on patent family members

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	9116378	AU	77439/91	AU	654131	EP	487661
AU	73964/91	AU	626511	AT	138954	BR	9101131
		CA	2021907	DE	69027303	EP	451425
		ES	2090115	JP	4249545	TR	26059
		US	5053246				
WO	8911500	AU	37420/89	AU	640345		
US	5494712	CA	2147486	EP	674722	JP	8505186
		WO	9414998				
EP	176636	DE	3482168				

END OF ANNEX